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(11) **EP 1 091 026 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
11.04.2001 Bulletin 2001/15

(51) Int. Cl.⁷: **D01F 1/09, D01F 8/12**

(21) Application number: **00121038.4**

(22) Date of filing: **27.09.2000**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **06.10.1999 JP 28546499**

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(54) **Electrically-conductive composite fiber**

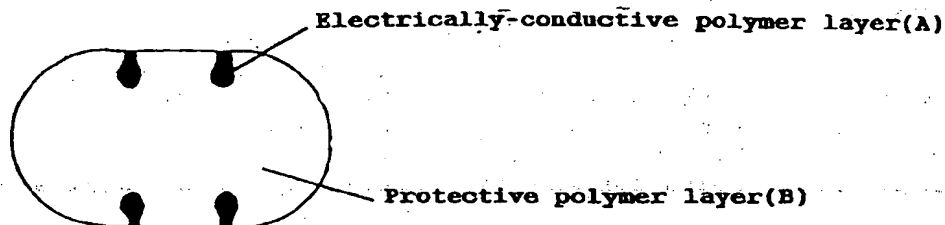
(57) To provide an electrically-conductive composite fiber which does not suffer component separation during spinning, retains its good initial conductive performance for a long period of time, and exhibits good color fastness. The electrically-conductive composite fiber is composed of an electrically-conductive polyamide layer (A) containing 15-50 wt% of electrically-conductive carbon black and a protective polymer layer (B) of polyamide of specific composition, wherein said electrically-conductive polyamide layer (A) exposes itself at the fiber surface such that the number of exposed parts is 3 or more and the length (L_1 μ m) of one exposed part

along the periphery of a cross section satisfies the expression below, and said protective polymer layer (B) covers not less than 60% of the periphery of the fiber cross section and accounting for 50-97 wt% of the total fiber weight.

$$0.1 \leq L_1 \leq L_2/10 \quad (1)$$

(where L_2 stands for the length (in μ m) of the periphery of a cross section of one filament.)

Fig. 1



Description

BACKGROUND OF THE INVENTION

1. Field of the Invention:

[0001] The present invention relates to a composite fiber with a good destaticizing property. More particularly, the present invention relates to an electrically-conductive composite fiber which suppresses dusting in practical use, keeps good conducting performance over a long period of time, and can be mixed with other fiber to give garments having good ironing resistance and good color fastness. Moreover, the present invention relates also to an electrically-conductive composite fiber which exhibits good destaticizing performance over a long period of time when used as a charging brush for copying machines and printers, thereby producing high-quality printed images over a long period of time, despite its low content of electrically-conductive carbon black.

2. Description of the Related Arts:

[0002] There have been proposed a variety of electrically-conductive fibers with a good destaticizing property. One of them is given electrical conductivity by metallic plating on the surface of a fiber lacking electrical conductivity. Another of them is made electrically-conductive by means of an electrically-conductive coating layer formed thereon from resin or rubber incorporated with electrically-conductive carbon black. Unfortunately, they need complex and difficult production processes or they easily lose electrical conductivity during scouring (involving chemical treatment) and in actual use (involving wearing and repeated washing).

[0003] Another example of electrically-conductive fiber is metallic fiber, such as steel fiber. Although metallic fiber is known for its good destaticizing property, it is expensive and incompatible with ordinary organic matters, which causes troubles in weaving and dying steps. Moreover, it easily breaks and drops during washing and its electrical conductivity gives an unpleasant feel and causes sparking and cloth melting.

[0004] Further another example of electrically-conductive fiber is one which is produced from a polymer containing electrically-conductive carbon black dispersed uniformly therein. A disadvantage of this type of fiber is difficulty in its production process due to a large amount of electrically-conductive carbon black contained therein. It is poor in yields and high in production cost. It is extremely poor in fiber properties and it can be produced only with difficulties by using a special process.

[0005] New ideas have been proposed in order to tackle these problems. For example, U.S. Patent No. 3,803,453 discloses a composite fiber of sheath-core type in which the core polymer contains an electrically-conductive carbon black and the sheath is made of an ordinary fiber-forming polymer. In addition, Japanese Patent Publication No. 44579/1978 discloses an electrically-conductive composite fiber in which the core containing an electrically-conductive carbon black is covered only partly by sheath.

[0006] The one disclosed in the U.S. Patent is limited in its core size (smaller than 50%) so that it exhibits necessary fiber properties. This leads to a thick sheath (which is non-conductive) and a core highly filled with carbon black. The one disclosed in the Japanese Patent, which is intended to solve this problem, is poor in chemical resistance and durability and liable to core-sheath separation because the core is not completely covered by the sheath. Moreover, Japanese Patent Laid-open No. 152513/1977 discloses a composite fiber of side-by-side configuration which is composed of a layer of electrically-conductive polymer containing an electrically-conductive carbon black and a layer of non-electrically-conductive polymer containing no carbon black, with the two polymers being of the same type. This electrically-conductive fiber is also poor in chemical resistance and durability because the layer containing an electrically-conductive carbon black exposes itself at its surface.

[0007] On the other hand, Japanese Patent Laid-open Nos. 147865/1978 and 34470/1979 disclose an electrically-conductive fiber which is composed of a fiber-forming polymer and a linear polymer containing an organic electrically-conductive substance streakily dispersed therein. This fiber is less liable to peeling and surface wearing and has improved wash resistance (durability) because its electrically-conductive component is enclosed therein.

[0008] The disadvantage of this fiber is low strength arising from the fact that the linear polymer containing an organic electrically-conductive substance is dispersed and mixed discontinuously in the lengthwise direction, without contribution to fiber strength, in the fiber-forming polymer which is completely incompatible with the linear polymer. In addition, this fiber fluctuates in electrical conductivity depending on how the electrically-conductive polymer is dispersed. This makes it difficult to control manufacturing conditions and product quality. In the case where a polymer is mixed with and dispersed in an incompatible polymer, the dispersed component is not completely enclosed in the matrix component but it partly exposes itself at the surface; therefore, the dispersed component (or the electrically-conductive polymer) will partly drop off. In addition, this fiber is poor in productivity because its production suffers excessively large ballooning which stains spinnerets and causes fiber breakage.

[0009] Other electrically-conductive composite fibers are disclosed in Japanese Patent Laid-open Nos. 134117/1979, 132624/1986, and 279416/1997. They are constructed such that the electrically-conductive polymer layer partly exposes itself at the fiber surface. They wear only a little by friction with metal in fiber production and fiber processing, and they prevent the constituent components from separating from each other and the electrically-conductive component from dropping off.

[0010] The conventional electrically-conductive composite fiber composed of an electrically-conductive polymer layer and a non-electrically-conductive polymer layer poses no problems during production but suffers the disadvantage of decreasing in conductivity due to peeling after prolonged use in the form of fiber product. The electrically-conductive composite fiber is usually mixed with ordinary fiber when it is used for garments such as uniforms. Such union fabrics are not satisfactory when dyed because the electrically-conductive fiber is poor in color fastness.

[0011] In the conventional technology of electrically-conductive fiber for garment use, no attention has been paid to the long-term durability of conductivity, peel resistance of constituent components, and performance in use.

[0012] There has not been any electrically-conductive composite fiber for non-garment applications which has such good properties as stable conductivity not affected by temperature (or environment), low starting voltage, good destaticizing performance at a high applied voltage, very little decrease in destaticizing performance after prolonged use, and ability to produce sharp images continuously over a long period of time.

OBJECT AND SUMMARY OF THE INVENTION

[0013] It is an object of the present invention to provide an electrically-conductive composite fiber which does not suffer wear or component separation during its production or its processing into fabrics but keeps its good initial performance even after its use (in the form of fabric) for a long period of time.

[0014] It is another object of the present invention to provide an electrically-conductive composite fiber which has such good color fastness that it causes no color migration to the other fiber, when mixing the electrically-conductive composite fiber and another fiber to make a mixed fabric and dyeing the fabric.

[0015] The present invention is directed to an electrically-conductive composite fiber composed of an electrically-conductive polymer layer (A) of thermoplastic polyamide containing 15-50 wt% of electrically-conductive carbon black and a protective polymer layer (B) of thermoplastic polyamide having a melting point not lower than 170°C, wherein said electrically-conductive polymer layer (A) exposes itself at three or more places on the fiber surface along the periphery of an arbitrary cross section such that the length (L_1 μm) of one exposed part satisfies the expression (1) below, said protective polymer layer (B) covers not less than 60% of the periphery of the fiber cross section and accounts for 50-97 wt% of the total fiber weight, and said thermoplastic polyamide constituting said protective polymer layer (B) is one which is synthesized from a dicarboxylic acid in which an aromatic dicarboxylic acid accounts for not less than 60 mol% and a diamine in which a C_{6-12} aliphatic alkylendiamine accounts for not less than 60 mol%.

$$0.1 \leq L_1 \leq L_2/10 \quad (1)$$

(where L_2 stands for the length (in μm) of the periphery of a cross section of one filament.)

[0016] In a preferred embodiment of the present invention, the electrically-conductive layer (A) contains at least two kinds of electrically-conductive carbon blacks differing in oil absorption such that the ratio of the oil absorption of the first carbon black to the oil absorption of the second carbon black is from 1.2 to 25, and has an electrical resistance R ($\Omega/\text{cm} \cdot \text{f}$) for an applied voltage of 100V, R satisfying the expression below.

$$\log R = 7.0 - 11.9 \quad (2)$$

[0017] The electrically-conductive composite fiber of the present invention can be used for garments (such as uniforms) as well as charging brushes and/or destaticizing brushes built into printers and copying machines.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

Fig. 1 is a sectional view showing a configuration of the electrically-conductive composite fiber according to the present invention.

Fig. 2 is a sectional view showing another configuration of the electrically-conductive composite fiber according to the present invention.

Fig. 3 is a sectional view showing another configuration of the electrically-conductive composite fiber according to the present invention.

Fig. 4 is a sectional view showing another configuration of the electrically-conductive composite fiber according to the present invention.

Fig. 5 is a sectional view showing another configuration of the electrically-conductive composite fiber according to the present invention.

Fig. 6 is a sectional view showing another configuration of the electrically-conductive composite fiber according to the present invention.

Fig. 7 is a sectional view showing another configuration of the electrically-conductive composite fiber according to the present invention.

Fig. 8 is a sectional view showing another configuration of the electrically-conductive composite fiber according to the present invention.

Fig. 9 is a sectional view showing a configuration of the electrically-conductive composite fiber in Comparative Example 3.

Fig. 10 is a sectional view showing a configuration of the electrically-conductive composite fiber in Comparative Example 4.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] According to the present invention, the electrically-conductive polymer layer (A) should contain, as one component thereof, electrically-conductive carbon black in an amount of 15-50 wt%, preferably 20-40 wt%. With a content less than 15 wt%, the electrically-conductive carbon black does not produce the desired conductivity and hence the electrically-conductive composite fiber does not exhibit satisfactory destaticizing performance. With a content in excess of 50 wt%, the effect of the electrically-conductive carbon black levels off and the polymer constituting the core is extremely poor in fluidity and spinnability.

[0020] Electrically-conductive carbon black should have "structure" (a chain-like structure of particles) so that it exhibits good electrical conductivity. Carbon black composed of dispersed particles is poor in electrical conductivity. In order to produce an electrically-conductive polymer, it is important to disperse an electrically-conductive carbon black into a base polymer without breaking the "structure".

[0021] A composite material containing electrically-conductive carbon black is considered to exhibit electrical conductivity through contact or tunnel effect between carbon black chains, probably the former dominating. The longer the carbon black chains and the higher the density of carbon black in a polymer, the higher the electrical conductivity owing to the high possibility of carbon black particles coming into contact with one another. The present inventors found that the electrical conductivity due to electrically-conductive carbon black is very small if the content is less than 15 wt% but it remarkably increases as the content increases to 20 wt% and levels off as the content exceeds 30 wt%.

[0022] The electrically-conductive composite fiber of the present invention should be composed of the electrically-conductive layer (A) and the protective layer (B) in a specific ratio. In other words, the former should account for 3 wt% or more and the latter should account for 97 wt% or less. Otherwise, the resulting composite fiber lacks stable structure for spinning. In addition, in the case where the composite fiber has a plurality of cores, the cores are discontinuous in the lengthwise direction. If the electrically-conductive layer (A) accounts for more than 50 wt%, the resulting composite fiber is poor in spinnability and drawability even though the protective polymer layer (B) has good fiber-forming properties.

[0023] Electrically-conductive carbon black impairs the spinnability of the electrically-conductive layer (A), and if the electrically-conductive layer (A) poor in spinnability accounts for more than half, the resulting composite fiber is poor in spinnability as a matter of course.

[0024] For this reason, the ratio of the electrically-conductive polymer layer (A) to the protective polymer layer (B) should be A:B = 3:97 - 50:50, preferably 7:93 - 35:65, by weight.

[0025] According to the present invention, the electrically-conductive composite fiber should be constructed such that the electrically-conductive polymer layer (A) partly exposes itself at the fiber surface at three or more places along the periphery of arbitrary cross section of the fiber. The number of such places should be not more than 10, preferably from 4 to 8.

[0026] In addition, the electrically-conductive polymer layer (A) should expose itself to such an extent that the length (L_1) of one exposed part is not smaller than 0.1 μm and not larger than $L_2/10$ measured in the circumferential direction of the fiber cross section, where L_2 is the length (in μm) of the periphery of the cross section of the composite fiber.

[0027] In the case that the length (L_1) is smaller than 0.1 μm even though the number of exposed parts is 3 or more, or in the case that the number of exposed parts is less than 3, the composite fiber does not produce stable conductivity because of the low probability of the electrically-conductive polymer coming into contact with the object in contact with the composite fiber. In contrast, if the length (L_1) exceeds ($L_2/10$), then the composite fiber present difficulties in the spinning process and is poor in wear resistance. Moreover, it permits the electrically-conductive polymer layer (A) and the protective polymer layer (B) to peel easily from each other, and it is poor in electrical conductivity.

[0028] According to the present invention, the protective polymer layer (B) should have a length which accounts for not less than 60%, preferably not less than 70%, of the length of the periphery of the fiber cross section. Otherwise, the composite fiber is poor in spinnability and strength.

[0029] The protective polymer layer (B) is important for the composite fiber to exhibit good spinnability, good properties, and good durability. The protective polymer layer (B) is formed from a fiber-forming thermoplastic polyamide having a melting point not lower than 170°C. This thermoplastic polyamide should be one which is composed of a dicarboxylic acid in which an aromatic dicarboxylic acid accounts for not less than 60 mol% and a diamine in which a C₆₋₁₂ aliphatic alkylenediamine accounts for not less than 60 mol%. This polyamide is characterized by its good heat resistance (particularly under wet heat condition) and good spinnability and ability to give fiber having high strength and good color fastness.

[0030] An example of the aromatic dicarboxylic acid is terephthalic acid, which is desirable from the standpoint of heat resistance. Other examples include isophthalic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,4-phenylenedioxydiacetic acid, 1,3-phenylenedioxydiacetic acid, diphenic acid, dibenzoic acid, 4,4'-oxydibenzoic acid, diphenylmethane-4,4'-dicarboxylic acid, diphenylsulfone-4,4'-dicarboxylic acid, and 4,4'-biphenyldicarboxylic acid. They may be used alone or in combination with one another. The content of the aromatic dicarboxylic acid in the dicarboxylic acid component should be not less than 60 mol%, preferably not less than 75 mol%.

[0031] Examples of dicarboxylic acids other than the above-mentioned aromatic dicarboxylic acids include aliphatic dicarboxylic acids (such as malonic acid, dimethylmalonic acid, succinic acid, 3,3-diethylsuccinic acid, glutaric acid, 2,2-dimethylglutaric acid, adipic acid, 2-methyladipic acid, trimethyladipic acid, pimelic acid, azelaic acid, sebacic acid, and suberic acid) and alicyclic dicarboxylic acids (such as 1,3-cyclopentanedicarboxylic acid and 1,4-cyclohexanedicarboxylic acid). They may be used alone or in combination with one another.

[0032] In addition, they may be used in combination with a polycarboxylic acid (such as trimellitic acid, trimesic acid, and pyromellitic acid) in an amount not harmful to spinning.

[0033] According to the present invention, the content of the aromatic dicarboxylic acid in the dicarboxylic acid component should preferably be 100% from the standpoint of heat resistance and fiber properties.

[0034] According to the present invention, not less than 60 mol% of the diamine component should be a C₆₋₁₂ aliphatic alkylenediamine. Examples of such aliphatic alkylenediamines include 1,6-hexanediamine, 1,8-octanediamine, 1,9-nonanediamine, 1,10-decanediamine, 1,11-undecanediamine, 1,12-dodecanediamine, 2-methyl-1,5-pentanediamine, 3-methyl-1,5-pentanediamine, 2,2,4-trimethyl-1,6-hexanediamine, 2,4,4-trimethyl-1,6-hexanediamine, 2-methyl-1,8-octanediamine, and 5-methyl-1,9-nonanediamine. Of these examples, 1,9-nonanediamine is preferable from the standpoint of heat resistance and fiber properties. It may be used in combination with 2-methyl-1,8-octanediamine.

[0035] The content of the aliphatic alkylenediamine in the diamine component should be not less than 60 mol%, preferably not less than 75%, particularly not less than 90 mol%.

[0036] Examples of diamines other than the above-mentioned aliphatic alkylenediamine include aliphatic diamines (such as ethylenediamine, propylenediamine, and 1,4-butanediamine), alicyclic diamines (such as cyclohexanediamine, methylcyclohexanediamine, isophoronediamine, norbornanedimethyldiamine, and tricyclodecanedimethyldiamine), and aromatic diamines (such as p-phenylenediamine, m-phenylenediamine, xylylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, and 4,4'-diaminodiphenylether). They may be used alone or in combination with one another.

[0037] In the case where 1,9-nonanediamine and 2-methyl-1,8-octanediamine are used in combination as the aliphatic alkylenediamine, their total amount should be 60-100 mol% of the diamine component and the molar ratio of the former to the latter should be 30:70 - 99:1, preferably 40:60 - 95:5.

[0038] The polyamide used in the present invention should preferably be one in which the molecular chain contains CONH units and CH₂ units in a ratio of 1/2 - 1/8, particularly 1/3 - 1/5.

[0039] The above-mentioned polyamide should have an intrinsic viscosity of 0.6-2.0 dl/g, preferably 0.6-1.8 dl/g, and more preferably 0.7-1.6 dl/g (measured at 30°C in conc. sulfuric acid), so that it has a melt viscosity suitable for spinning and gives fibers having good properties and good heat resistance.

[0040] In addition, the above-mentioned polyamide should preferably have molecular chains whose terminal groups are partly blocked by a blocking agent. The ratio of blocked terminal groups should be not less than 10%, preferably not less than 40%, and more preferably not less than 70%.

[0041] The above-mentioned polyamide may be produced by any known method applicable to crystalline polyamides. Examples of such methods include solution polymerization or interfacial polymerization which starts with an acid chloride and a diamine, and melt polymerization or solid phase polymerization which starts with a dicarboxylic acid (or an alkyl ester thereof) and a diamine.

[0042] The above-mentioned polyamide adheres well to the electrically-conductive polymer layer (A) which is one of the important constituents in the present invention. In addition, it is immune to interfacial peeling and is desirable from

the standpoint of heat resistance and fiber properties.

[0043] According to the present invention, the electrically-conductive polymer layer (A) is formed from a polymer which is explained in the following.

[0044] According to the present invention, it is important to use a thermoplastic polyamide as the polymer which constitutes the electrically-conductive polymer layer (A). Examples of this thermoplastic polyamide include nylon-12, nylon-11, nylon-6, nylon-66, and nylon elastomer. They may be replaced by the above-mentioned polyamide constituting the protective layer (B).

[0045] Electrically-conductive fiber is usually used in the form of working wear for work in an environment where static build-up causes explosion or charging brushes for copying machines. Repeated bending, stretching, and rubbing in their prolonged use cause damage (such as cracking) to the electrically-conductive layer, thereby deteriorating the destaticizing performance. There is no way to recover such damage, and it is necessary to replace damaged items in a short period of time.

[0046] The present inventors investigated the dispersion of electrically-conductive carbon black into a variety of polymers. It was found that polyamides having polar groups are highly compatible with electrically-conductive carbon black and retain their high fluidity even after incorporation with a large amount of electrically-conductive carbon black. In other words, polyamides can be made into compounds having good electrical conductivity and good fluidity. Such compounds are also superior in mechanical properties because of good adhesion between polyamide and electrically-conductive carbon black.

[0047] The foregoing is true only for polyamides. Polyesters rapidly increases in viscosity and loses fluidity as it is incorporated with electrically-conductive carbon black even though the mixing ratio is low. In other words, polyesters cannot be made into an electrically-conductive polymer that has desired electrical-conductivity and desired spinnability. It is not competitive with polyamide resins.

[0048] As compared with polyesters, polyolefins retains slightly better fluidity even after incorporation with electrically-conductive carbon black and hence it can be made easily into an electrically-conductive polymer. Unfortunately, the resulting compound is much poorer in mechanical properties than the compound of polyamides because polyolefins is poor in adhesion to electrically-conductive carbon black. Therefore, the compound of polyolefins will present difficulties such as breakage of the electrically-conductive polymer layer in processing into composite fiber.

[0049] It is concluded from the foregoing that thermoplastic polyamides are most suitable as the polymer to be made into the electrically-conductive polymer layer by incorporation with electrically-conductive carbon black.

[0050] According to the present invention, the electrically-conductive composite fiber should have an electrical resistance R ($\Omega/\text{cm} \cdot f$) which can be varied depending on applications. If the electrically-conductive composite fiber is to be used for garments or charging brushes, it should have an electrical resistance R ($\Omega/\text{cm} \cdot f$), at an applied voltage of 100V, which satisfies the expression below.

$$\log R = 7.0 - 11.9$$

In particular, the one for charging brushes should preferably a value of R ($\Omega/\text{cm} \cdot f$) such that $\log R = 8.5 - 11.5$.

[0051] To meet requirements for such electrical resistance characteristics in the present invention, it is desirable to use two kinds of electrically-conductive carbon blacks in combination which differ in oil absorption. A first one may have an oil absorption of 130-350 cc/100 g, and a second one may have an oil absorption of 15-130 cc/100 g. The ratio of the former oil absorption to the latter oil absorption should preferably be from 1.2 to 25. The oil absorption is determined by measuring the maximum amount (in cc) of linseed oil absorbed by 100 g of carbon black.

[0052] The above-mentioned two kinds of electrically-conductive carbon blacks differ also in resistivity. The former may have a resistivity of $10^{-3} - 10^2 \Omega \cdot \text{cm}$ and the latter may have a resistivity of $10^0 - 10^6 \Omega \cdot \text{cm}$.

[0053] The mixing ratio of the former to the latter should preferably be from 10:1 to 1:10 so that the resulting mixture exhibits desired conductivity.

[0054] The electrically-conductive composite fiber of the present invention may be produced in any manner which is not specifically restricted. For example, it may be produced by melt-spinning and ensuing drawing with an apparatus for multicore-sheath composite fiber. Ordinary melt-spinning may be replaced by high-speed spinning which obviates the necessity of drawing. In the process of melt-spinning, it is important to adjust the relative positions of the inlets for the electrically-conductive polymer and the protective polymer so that the electrically-conductive polymer layer (A) exposes itself at the fiber surface as desired and the ratio of the two polymers are adequately controlled.

[0055] For the electrically-conductive composite fiber of the present invention to have improved drawability, it is desirable to incorporate the protective layer (B) with not more than 5 wt% of inorganic fine powder having an average particle diameter not larger than 0.5 μm .

[0056] The electrically-conductive composite fiber of the present invention which is produced in the above-mentioned manner may have any monofilament fineness which is not specifically restricted. Common fineness ranges from 2 to 34 dtex.

[0057] According to the present invention, the electrically-conductive layer (A) partly exposes itself at the fiber surface so that it exhibits conductivity at a low voltage generated by friction. This effect is achieved only when the electrically-conductive polymer layer (A) is combined with the protective polymer layer (B) specified above.

[0058] The composite fiber of the present invention may have any cross section which is not specifically restricted so long as the electrically-conductive polymer layer (A) exposes itself as mentioned above. Examples of the cross section are shown in Figs. 1 to 8. A cross section shown in Fig. 3 is most desirable because the four core components are arranged at equal intervals along the periphery of the cross section and each core component exposes itself at the fiber surface.

[0059] The electrically-conductive composite fiber mentioned above will find use as a charging brush or a destaticizing brush for copying machines and printers because of its long-lasting good destaticizing performance as well as its good fiber characteristics. It will also find use in the field of garment (such as working wear and uniform to avoid static electrification) owing to its good color fastness.

EXAMPLES

[0060] The invention will be described in more detail with reference to the following examples, which are not intended to restrict the scope thereof. Characteristic properties of each sample were measured in the following manner.

(Electrical resistance R)

[0061] A sample of the electrically-conductive composite fiber (monofilament) is held between parallel clip electrodes. A dc voltage of 25-500V is applied to the sample, and a current flowing through the sample is measured with a voltammeter. The electrical resistance of the sample is calculated according to Ohm's law from the voltage and the current at that voltage. The electrical resistance specified in the present invention is one which is measured at 100V.

(Amount of charge)

[0062] A sample is rubbed with a fabric of acrylic fiber at 20°C and 40% RH, and the amount of charge generated is measured with a simple Faraday gauge conforming to JIS L1094.

(Color fastness to washing)

[0063] A specimen (measuring 100 × 40 mm) is cut out of the fabric dyed under the condition shown in Example 1. To the surface of the specimen are sewn side by side two pieces of nylon cloth (measuring 50 × 40 mm). The specimen is washed according to JIS L0844-1997, Method A-2.

(1) Liquid soiling is judged according to JIS L0801-9 by observing the liquid remaining after washing which has been placed in a porcelain beaker (2 × 4 × 1 cm).

(2) Soiling of the nylon cloth is judged according to JIS L0801-9.

(Evaluation of printed images)

[0064] A copying machine with dc bias voltage is run, with a charging brush under test turning in the direction opposite to that of the photoreceptor. Printed images are evaluated after initial runs and continued runs (10,000 copies). Criteria for evaluation are as follows.

(1) Evaluation after initial runs

[0065]

○ : Images are uniform and clear.

Δ : Images have some traces due to anomalous discharge.

X : Images are blurred, with apparent streaky marks.

(2) Evaluation after continued runs

[0066]

- 5 ○ : Images are as uniform and clear as those after initial runs.
 Δ : Images have some traces due to anomalous discharge.
 X : Images are blurred, with apparent streaky marks.

Referential Examples 1 and 2

(Preparation of thermoplastic polyamide)

[0067] The following raw materials were placed in a 20-liter autoclave.

- 15 Terephthalic acid: 19.5 mol
 1,9-nonanediamine: 10.0 mol
 2-methyl-1,8-octanediamine: 10.0 mol
 Benzoic acid: 1.0 mol
 Sodium hypophosphite monohydrate: 0.06 mol (0.1 wt% of raw materials)
 Distilled water: 2.2 liters

[0068] The atmosphere in the autoclave was replaced with nitrogen. The content of the autoclave was stirred at 100°C for 30 minutes, and then the temperature in the autoclave was raised to 210°C over 2 hours and the pressure in the autoclave was raised to 22 kg/cm² (2.16×10^6 Pa) in the same period. Reaction was continued for 1 hour at this temperature and pressure. The temperature was raised to 230°C and this temperature was maintained for 2 hours. Reaction was continued at a constant pressure of 22 kg/cm² (2.16×10^6 Pa), which was maintained by discharging steam from the autoclave. The pressure was reduced to 10 kg/cm² (9.81×10^5 Pa) over 30 minutes. Reaction was continued for 1 hour at this pressure. Thus there was obtained a prepolymer. This prepolymer was dried at 100°C for 12 hours under reduced pressure. The resulting product was crushed into particles smaller than 2 mm.

[0069] The crushed product underwent solid phase polymerization at 230°C and 0.1 mmHg (13.3 Pa) for 10 hours. Thus there was obtained a desired polyamide, which has an intrinsic viscosity of 0.9 and a CONH/CH₂ ratio of 1/3.9, as shown in Table 1.

Table 1

		Referential Example 1 PA9MT	Referential Example 2 PA9T
Composition	Terephthalic acid (mol)	19.5	19.4
	1,9-nonanediamine (mol)	10.0	20.0
	2-methyl-1,8-octanediamine(mol)	10.0	-
	Benzoic acid (mol)	1.0	1.2
NaH ₂ PO ₂ · H ₂ O(mol)		0.06	0.06
Intrinsic viscosity		0.9	0.8
CONH/CH ₂ ratio		1/3.9	1/4.5

Example 1

[0070] This example demonstrates the performance of an electrically-conductive composite fiber composed of an electrically-conductive polymer component (A) and a protective polymer component (B). Component (A) is nylon-6 containing 35 wt% of electrically-conductive carbon black (with oil absorption of 115 cc/100 g). Component (B) is the thermoplastic polyamide (PA9MT) obtained in Referential Example 1, whose properties are shown in Table 1. The components A and B in a ratio of 13/87 by weight were spun into a composite fiber of core-sheath type having the cross section as shown in Fig. 3. (This composite fiber has four cores which expose themselves at the fiber surface.) Spinning was followed by drawing. Thus there was obtained the desired electrically-conductive composite fiber having a fineness

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of 25 denier/4 f (27.8 dtex/4f) and also having $L_2 = 88 \mu\text{m}$, which is the length of the periphery of the cross section of one filament. There was no problem in the spinning process. The thus obtained electrically-conductive composite fiber has the electrically-conductive layer (A) which is uniformly continuous in the fiber axial direction. The electrically-conductive layer (A) exposes itself at four places in the fiber surface. The length (L_1) of each exposed part is $0.6 \mu\text{m}$ in the peripheral direction of the cross section of the fiber. In other words, the composite fiber has L_1 and L_2 which satisfy the condition $0.1 \leq L_1 \leq L_2/10$. In addition, the composite fiber invariably has an electrical resistance of $2 \times 10^8 \Omega / \text{cm} \cdot f$ (log $R = 8.3$) at 100V. It exhibits good electrical conductivity at a low voltage applied.

[0071] The thus obtained composite fiber was covered with polyester/cotton (65/35) blended yarn. A 2/1 twill (80 warps/inch and 50 wefts/inch) was woven from polyester/cotton (65/35) blended yarn having a cotton yarn number of 20S/2, one pick per 80 warps being the covered yarn mentioned above. The polyester and cotton in the twill were dyed sequentially in the following manner.

(1) Dyeing of polyester

(Dyeing)

[0072]

Disperse dye:	Dianix Blue BG-FS	3% omf
Dispersant:	Disper TL	1 g/L
	Acetic acid (50%)	0.5 cc/L
Bath ratio:	1:50	
Dyeing temperature \times time :	130°C \times 40 minutes	

(Reduction clearing)

[0073]

Hydrosulfite	1 g/L
NaOH	1 g/L
Amiladine D	1 g/L

[0074] Reduction clearing was followed by cold water washing.

(2) Dyeing of cotton

(Dyeing)

[0075]

Reactive dye:	Sumifix Supra BRF 150% gran:	2% omf
	Sodium sulfate:	40 g/L
Bath ratio:	1:50	

[0076] The fabric is kept in the bath at 30°C for 20 minutes. Then the bath temperature is raised to 70°C over 20

minutes. After standing at 70°C for 20 minutes, the bath is given Na₂CO₃ (20 g/L). Dyeing is carried out for 20 minutes. Soaping with marseilles soap (2 g/L) and Na₂CO₃ (2 g/L) is carried out at 90°C for 20 minutes. Dyeing is completed by cold water washing.

[0077] The fabric was found to have a charge of 3.5 $\mu\text{C}/\text{m}^2$. After actual wearing for 2 years and repeated washing (about 250 times), the fabric had a charge of 4.8 $\mu\text{C}/\text{m}^2$. This indicates that the fabric has good destaticizing performance and good durability. See Tables 2 and 3. It meets the requirement for the standard value (lower than 7 $\mu\text{C}/\text{m}^2$) in "Recommended Practice for Protection Against Hazards Arising out of Static Electricity in General Industries" issued by Technology Institute of Industrial Safety.

Table 2

	Electrically-conductive polymer layer (A)				Protective polymer layer (B)				Ratio of A/B (wt%)
	Electrically-conductive carbon blacks (α and β)			Matrix polymer	Carbon black (wt%)	Matrix polymer	Fine powder	Amount added (wt%)	
	Oil absorption of α (cc/100 g)	Oil absorption of β (cc/100 g)	Mixing Ratio (α/β)						
Example 1	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	13/87
Example 2	115	—	—	Nylon-6	35	PA9T	TiO ₂	0.5	13/87
Example 3	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	13/87
Example 4	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	10/90
Example 5	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	25/75
Example 6	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	13/87
Example 7	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	13/87
Example 8	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	13/87
Example 9	115	—	—	Nylon-8	35	PA9MT	SiO ₂	2.0	13/87
Example 10	115	—	—	Nylon-12	35	PA9MT	TiO ₂	0.5	13/87
Example 11	180	80	2/1	Nylon-6	35	PA9MT	—	—	13/87
Example 12	180	40	1/1	Nylon-6	40	PA9MT	TiO ₂	0.5	13/87
Example 13	180	40 *	1/2	Nylon-6	40	PA9MT	TiO ₂	0.5	13/87
Example 14	115	40 *	1/2	Nylon-6	40	PA9MT	TiO ₂	0.5	13/87
Comp. Ex. 1	115	—	—	Polyethylene	35	PA9MT	TiO ₂	0.5	13/87
Comp. Ex. 2	115	—	—	Polyester	25	PA9MT	TiO ₂	0.5	13/87
Comp. Ex. 3	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	25/75
Comp. Ex. 4	115	—	—	Nylon-6	35	PA9MT	TiO ₂	0.5	50/50
Comp. Ex. 5	180	40	1/1	Nylon-6	40	PA9MT	TiO ₂	0.5	13/87
Comp. Ex. 6	—	40	—	Nylon-6	40	PA9MT	TiO ₂	0.5	13/87
Comp. Ex. 7	115	—	—	Nylon-6	35	Nylon-6	—	—	13/87

* Insulating carbon black.

Table 3

	Cross section	Number of exposed parts	Length of exposed parts L_1 (μm)	Length of periphery of cross section L_2 (μm)	Electrical resistance R ($\Omega/\text{cm} \cdot \eta$)	$\log R$	Destatizing performance of fabric		Evaluation of Images		Color fastness (class)		Spinnability
							Initial charge ($\mu\text{C}/\text{m}^2$)	Charge after 2 years* ($\mu\text{C}/\text{m}^2$)	Initial Images	Images after 10,000 runs	Soiling of liquid	Soiling of fabric	
Example 1	Fig. 3	4	0.6	88	2×10^9	8.3	3.5	4.8	—	—	4.5	4.5	○
Example 2	Fig. 3	4	0.6	88	3×10^9	8.5	3.3	4.5	—	—	5	5	○
Example 3	Fig. 3	4	1.5	88	2×10^9	8.3	3.5	4.7	—	—	4.5	4.5	○
Example 4	Fig. 3	4	0.2	88	2×10^9	8.3	3.4	4.8	—	—	4.5	4.5	○
Example 5	Fig. 3	4	3.5	88	2×10^9	8.3	3.7	5.1	—	—	4.5	4.5	○
Example 6	Fig. 1	4	1.0	102	3×10^9	8.5	3.5	4.7	—	—	4.5	4.5	○
Example 7	Fig. 6	4	0.3	117	5×10^9	8.7	3.1	4.3	—	—	4.5	4.5	○
Example 8	Fig. 2	3	0.6	88	2×10^9	8.3	3.4	4.6	—	—	4.5	4.5	○
Example 9	Fig. 3	4	0.6	88	2×10^9	8.3	3.6	4.9	—	—	4.5	4.5	○
Example 10	Fig. 3	4	2.0	88	1×10^9	8.0	4.0	5.2	—	—	4.5	4.5	○
Example 11	Fig. 3	4	0.6	88	1×10^9	9.0	—	—	○	○	—	—	○
Example 12	Fig. 3	4	0.6	88	2×10^{10}	10.3	—	—	○	○	—	—	○
Example 13	Fig. 3	4	0.6	88	7×10^{10}	10.8	—	—	○	○	—	—	○
Example 14	Fig. 3	4	0.6	88	2×10^{11}	11.3	—	—	○	○	—	—	○
Comp. Ex. 1	Fig. 3	4	0.8	90	9×10^7	7.9	3.7	11.0	—	—	4.5	4.5	○
Comp. Ex. 2	Fig. 3	4	0.6	85	—	—	—	—	—	—	—	—	x
Comp. Ex. 3	Fig. 3	4	9.0	88	2×10^9	8.3	6.5	10.5	—	—	4.5	4.5	△-x
Comp. Ex. 4	Fig. 3	4	0.6	88	—	—	—	—	—	—	—	—	x
Comp. Ex. 5	Fig. 10	0	—	—	7×10^{12}	12.8	—	—	△-x	x	—	—	○
Comp. Ex. 6	Fig. 3	4	0.6	88	4×10^{12}	12.6	—	—	x	x	—	—	○
Comp. Ex. 7	Fig. 3	4	0.6	88	3×10^9	8.5	3.7	6.2	—	—	1.2	1.2	○

* After 250 washings

Example 2

[0078] The same procedure as in Example 1 was repeated except that the protective polymer component (B) was replaced by the thermoplastic polyamide (PA9T) in Table 2 which was prepared in Referential Example 2. This polymer exhibited good spinnability and the resulting fabric also exhibited good destaticizing performance and good durability, with the amount of charge (initial and after 250 washings) meeting requirements for standard values. See Tables 2 and 3.

Examples 3 to 5

[0079] The same procedure as in Example 1 was repeated except that the ratio (A/B) and/or the length of exposed part were changed as shown in Tables 2 and 3. The polymer exhibited good spinnability and the resulting fabric also exhibited good destaticizing performance and good durability, with the amount of charge (initial and after 250 washings) meeting requirements for standard values. See Tables 2 and 3.

Examples 6 to 8

[0080] The same procedure as in Example 1 was repeated except that the cross section of the fiber was changed to those shown in Fig. 1 (Example 6), Fig. 6 (Example 7), and Fig. 2 (Example 8). The polymer exhibited good spinnability and the resulting fabric also exhibited good destaticizing performance and good durability, with the amount of charge (initial and after 250 washings) meeting requirements for standard values. See Tables 2 and 3.

Examples 9 and 10

[0081] The same procedure as in Example 1 was repeated except that the protective polymer layer was incorporated with 2.0 wt% of SiO₂ fine powder (in Example 9) or the electrically-conductive matrix polymer was replaced by nylon-12 (in Example 10). The polymer exhibited good spinnability and the resulting fabric also exhibited good destaticizing performance and good durability, with the amount of charge (initial and after 250 washings) meeting requirements for standard values. See Tables 2 and 3.

Comparative Examples 1 to 4

[0082] Electrically-conductive composite fibers as shown in Tables 2 and 3 were prepared in the same way as in Example 1. They were poor in durability of destaticizing performance and spinnability. See Tables 2 and 3.

Example 11

[0083] The same procedure as in Example 1 was repeated except that the electrically-conductive polymer component (A) was replaced by nylon-6 incorporated with 35 wt% of two kinds of electrically-conductive carbon blacks differing in electrical conductivity (one having an oil absorption of 180 cc/100 g and the other having an oil absorption of 80 cc/100 g, with the mixing ratio of the former to the latter being 2/1). There was obtained electrically-conductive composite fiber having a fineness of 25 denier/4f (27.8 dtex/4f), with L₂ being 88 μm (length of periphery of cross section of one filament). The polymer was good in spinnability. The resulting electrically-conductive composite fiber has the electrically-conductive polymer layer (A) which is continuous in the direction of the fiber axis. The electrically-conductive polymer layer (A) exposed itself at the fiber surface and the number of exposed parts was four. The length (L₁) of each exposed part was 0.6 μm. Thus the composite fiber meets the condition of $0.1 \leq L_1 \leq L_2/10$. In addition, the composite fiber had an electrical resistance of $1 \times 10^9 \Omega/\text{cm} \cdot f$ (or $\log R = 9.0$) at 100V. In other words, it has good conductivity at a low applied voltage.

[0084] The thus obtained electrically-conductive composite fiber was made into a pile fabric having a density of 50,000 fibers/in². This pile fabric was used as a conductive brush for a copying machine. It gave good printed images free of traces due to anomalous discharge. It exhibited good durability and gave good printed images even after 10,000 runs. Refer to Tables 2 and 3 for composition, fiber form, spinnability, electrical resistance, and image evaluation.

Examples 12 to 14

[0085] The same procedure as in Example 11 was repeated except that changes were made in the kind of carbon black, the mixing ratio of carbon black, and the amount of carbon black added to the matrix polymer. The resulting polymer was good in spinnability and the fabric made from the composite fiber gave good printed images. See Tables 2

and 3.

Comparative Examples 5 and 6

- 5 [0086] Samples of electrically-conductive composite fiber as shown in Table 2 were prepared. Charging brushes made from them gave poor printed images when evaluated in the same way as in Example 11.

[Effect of the invention]

- 10 [0087] The present invention provides an electrically-conductive composite fiber which is formed in a specific way from a polyamide containing a specific amount of electrically-conductive carbon black and a thermoplastic polyamide of specific composition. The composite fiber finds use as garments and charging brushes for copying machines which keep good destaticizing performance for a long period of time in practical use. In addition, the composite fiber exhibits good color fastness and causes no sweating when dyed with other fiber.

Claims

- 15 1. An electrically-conductive composite fiber composed of an electrically-conductive polymer layer (A) of thermoplastic polyamide containing 15-50 wt% of electrically-conductive carbon black and a protective polymer layer (B) of thermoplastic polyamide having a melting point not lower than 170°C, wherein said electrically-conductive polymer layer (A) exposes itself at three or more places on the fiber surface along the periphery of an arbitrary cross section such that the length (L_1 , μm) of one exposed part satisfies the expression (1) below, said protective polymer layer (B) covers not less than 60% of the periphery of the fiber cross section and accounts for 50-97 wt% of the total fiber weight, and said thermoplastic polyamide constituting said protective polymer layer (B) is one which is synthesized from a dicarboxylic acid in which an aromatic dicarboxylic acid accounts for not less than 60 mol% and a diamine in which a C_{6-12} aliphatic alkylenediamine accounts for not less than 60 mol%.

$$0.1 \leq L_1 \leq L_2/10 \quad (1)$$

30 (where L_2 stands for the length (in μm) of the periphery of a cross section of one filament.)

2. An electrically-conductive composite fiber as defined in Claim 1, wherein the electrically-conductive layer (A) contains at least two kinds of electrically-conductive carbon blacks differing in oil absorption and has an electrical resistance R ($\Omega/\text{cm} \cdot f$) for an applied voltage of 100V, R satisfying the expression below.

$$\log R = 7.0 - 11.9 \quad (2)$$

3. An electrically-conductive composite fiber as defined in Claim 2, wherein the electrically-conductive layer (A) contains two kinds of electrically-conductive carbon blacks differing in oil absorption such that the ratio of the oil absorption of the first carbon black to the oil absorption of the second carbon black is from 1.2 to 25.

4. An electrically-conductive composite fiber as defined in any of Claims 1 to 3, wherein the protective polymer layer (B) contains not more than 5 wt% of inorganic fine powder having an average particle diameter not larger than 0.5 μm .

Fig. 1

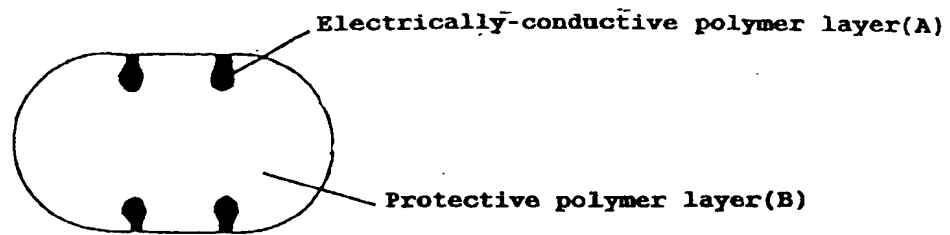


Fig. 2

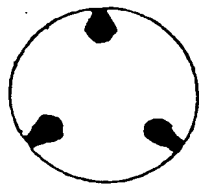


Fig. 3

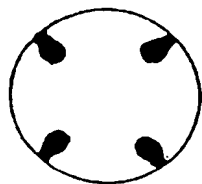


Fig. 4

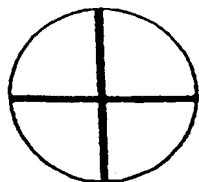


Fig. 5

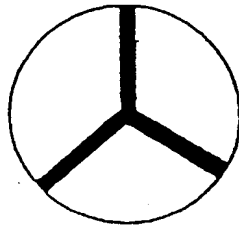


Fig. 6

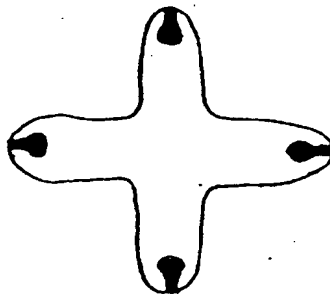


Fig. 7

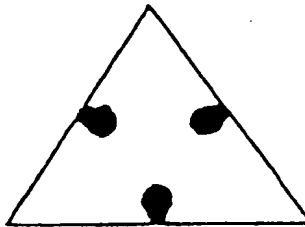


Fig. 8

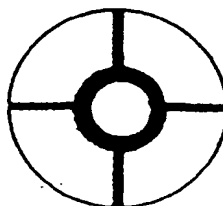


Fig. 9

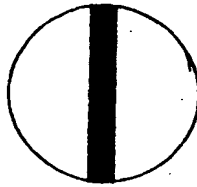
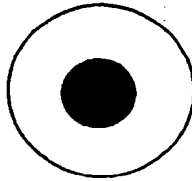


Fig. 10





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EUROPEAN SEARCH REPORT

Application Number
EP 00 12 1038

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 076 (C-0809), 21 February 1991 (1991-02-21) & JP 02 300317 A (KURARAY CO LTD), 12 December 1990 (1990-12-12) * abstract *	1-4	D01F1/09 D01F8/12
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 437 (C-0984), 11 September 1992 (1992-09-11) & JP 04 153306 A (KURARAY CO LTD), 26 May 1992 (1992-05-26) * abstract *	1-4	
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) & JP 09 013222 A (KURARAY CO LTD), 14 January 1997 (1997-01-14) * abstract *	1-4	
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 01, 30 January 1998 (1998-01-30) & JP 09 256219 A (KURARAY CO LTD), 30 September 1997 (1997-09-30) * abstract *	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.7) D01F
A	EP 0 929 011 A (XEROX CORP) 14 July 1999 (1999-07-14) * the whole document *	2,3	
A	EP 0 257 599 A (KONISHIROKU PHOTO IND) 2 March 1988 (1988-03-02) * the whole document *	2,3	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 January 2001	Examiner Tarrida Torrell, J
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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EUROPEAN SEARCH REPORT

Application Number
EP 00 12 1038

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 11, 26 December 1995 (1995-12-26) & JP 07 228776 A (KURARAY CO LTD), 29 August 1995 (1995-08-29) * abstract *	4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 January 2001	Examiner Tarrida Torrell, J
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.92 (P04C01)

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ON EUROPEAN PATENT APPLICATION NO.**

EP 00 12 1038

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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24-01-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 02300317 A	12-12-1990	JP 2833780 B	09-12-1998
JP 04153306 A	26-05-1992	JP 2801386 B	21-09-1998
JP 09013222 A	14-01-1997	NONE	
JP 09256219 A	30-09-1997	NONE	
EP 0929011 A	14-07-1999	US 5998010 A JP 2000075695 A	07-12-1999 14-03-2000
EP 0257599 A	02-03-1988	JP 2018318 C JP 7046419 B JP 63055722 A DE 3789130 D DE 3789130 T US 4812358 A	19-02-1996 17-05-1995 10-03-1988 31-03-1994 26-05-1994 14-03-1989
JP 07228776 A	29-08-1995	NONE	